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PROPERTIES OF INORGANIC POLYMER CEMENT FROM FERRIC AND FERROUS VITRIFIED RESIDUES OF PLASMA GASIFICATION

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Introduction

Climate change and resource scarcity pose a need to look for a sustainable supply of raw materials and energy. Plasma gasification is an emerging technology for energy production from refuse derived fuel (RDF). In the process, the RDF is converted to form a synthetic gas (syngas) that can be subsequently used for electricity production.¹ At the elevated temperatures of the process, the inorganic ash fraction of the RDF is molten and a vitreous residue, a glass, is formed which currently has limited application. Previous work has indicated that – when of appropriate chemistry and glass content – the glass can be applied as a raw material for the synthesis of inorganic polymer (IP) cement.² The IP cement is produced through milling and subsequent dissolution/polymerisation of the glass in an alkali-silicate solution. Good properties can be obtained, e.g. regarding strength, also if the glass is relatively poor in Al but rich in Fe.³

The current paper investigates the relation of the Fe oxidation state (ferric Fe³⁺ versus ferrous Fe²⁺) of the glass with the properties of the resulting IP cement. Depending on the plasma gasification process conditions, Fe can be present as Fe²⁺ (reduced glass), as Fe³⁺ (oxidized glass), although both forms can occur together⁴ and this is almost always the case. It is known that Fe²⁺ and Fe³⁺ behave differently in a silicate network, due to their differing size and charge. Oxidized and reduced glasses could thus possess differing dissolution, condensation and polymerisation behaviour in IP cements. When looking at literature on inorganic polymerisation of Fe-rich precursors, most studies are performed on residues of pyrometallurgical processes, e.g. slags from non-ferrous metal production.⁵⁻⁶ In all these slags Fe is present (predominantly) as Fe²⁺. In many cases, IP binders with good workability, setting and mechanical properties can be synthesised, even for precursors with only low contents of Al. However when looking at more fundamental studies, focus has been

on precursors containing Fe^{3+} rather than Fe^{2+} . The inorganic polymerisation of raw materials containing predominantly Fe^{3+} has been investigated in: (1) mixtures of Fe-nitrates or Fe-hydroxides with metakaolin and K-silicate;⁷ (2) mixtures of poorly crystalline $\text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2$ powders with K-silicate;⁸ (3) mixtures of synthetically produced glasses containing predominantly Fe^{3+} , minor Fe^{2+} and Al with Na-silicate;^{2,3} (4) mixtures of synthetically produced glasses containing Fe^{3+} , small amounts of Fe^{2+} but totally lacking Al.⁹ The properties of the synthesised IP vary, with hardening only occurring after one year in some cases,⁸ whereas elsewhere, IPs from Fe^{3+} -rich precursors containing no Al, have even improved mechanical properties compared to identical IPs in which Fe is replaced by Al.⁹ The large differences in properties as documented in these studies are attributed, among other, to the degree of reactivity (crystalline versus glassy) and the differing chemistry (e.g. ratios of Si/Fe/Ca) of the precursors. From the abovementioned studies, it was suggested that Fe^{3+} can be either present in oxyhydroxide precipitates (as a separate phase outside of the IP structure), or incorporated in the IP framework. For Fe^{2+} , there is still uncertainty with regards to its behaviour. Lemougna et al.¹⁰ observed the formation of a distorted tetrahedral or 5-coordinated site containing Fe^{3+} , but with Fe being derived from dissolved Fe^{2+} from the mineral augite. Apart from this, little is known about how Fe^{2+} is incorporated in the IP framework.

Synthesis of “oxidized” and “reduced” glass

The aim of the current study was to study the role of Fe oxidation state in Fe-rich glasses on the IP properties. Two glasses, comparable in composition and assemblage of crystal phases/glass content, but with differing Fe oxidation state were synthesised. Inorganic polymers were produced from both glasses in an identical way and setting behaviour and mechanical properties were investigated. Lab scale glass synthesis was performed using a powder mix composed of an existing plasma gasification residue that was adjusted in composition through addition of synthetic oxides. The following start composition was used in wt.%: CaO: 21.5; Fe_2O_3 : 22.0; Al_2O_3 : 11.8; SiO_2 : 33.4; MgO: 3.4; Na_2O : 3.6; TiO_2 : 1.6; Others: 2.7. The glasses were synthesised by melting the powder mix at 1450°C in an alumina crucible. Gas-melt equilibrium in a plasma gasification/melting process was mimicked through bubbling a gas through the melt for 1h at a rate of 60 L/h. Two conditions were applied: (1) equilibrium with a reducing gas (68 % CO – 32 % CO_2) and (2) equilibrium with an oxidising gas (air). The glass was produced by dipping a steel bar in the melt and quenching the bar covered with the melt in a water tank to obtain a nearly completely glassy phase and prevent $\text{Fe}^{2+}/\text{Fe}^{3+}$ conversion during solidification.

High temperature modelling of the system (using FactSage software) shows that under equilibrium with both gasses at 1450 °C, the mixtures are completely molten. In equilibrium with the reducing gas, Fe is predominantly present in its bivalent form (97 % Fe in FeO and 3 % Fe in Fe₂O₃). Under oxidising conditions, in equilibrium with air, Fe is predominantly present in its trivalent form, but substantial amounts of bivalent Fe are also present (77.4 % Fe in Fe₂O₃ and 22.6 % Fe in FeO).

Glass characterisation

The composition of the resulting glasses, obtained by XRF analysis, is shown in Table 1. FeO and Fe₂O₃ are calculated using the distribution calculated from the high temperature modelling. The composition of both glasses is similar, with the main difference in the Al₂O₃ content, which is also substantially higher compared to the Al content of the start mixture. This difference is explained by dissolution of Al from the crucible.

Table 1: XRF analyses. Cal. = calculated using high temperature modelling data

Wt.%	SiO ₂	Fe _{tot}	FeO _{cal.}	Fe ₂ O _{3cal.}	CaO	Al ₂ O ₃	MgO	Na ₂ O	TiO ₂	Others
Reduced glass	35.6	16.2	20.2	0.7	15.1	15.0	2.7	3.0	1.5	6.1
Oxidized glass	34.3	17.3	5.0	19.2	15.0	13.1	2.6	2.9	1.4	6.4

Quantitative XRD analysis (using Rietveld analysis and an internal ZnO standard to calculate the glass content) showed that the quenching procedure resulted in a nearly completely glassy phase. In the oxidised sample 4 wt.% of magnetite (Fe⁺²Fe⁺³₂O₄) was identified as the only crystalline phase, confirming the co-existence of Fe²⁺ and Fe³⁺. In the reduced sample only traces of magnetite were identified (0.2 wt.%). High temperature modelling confirms the formation of magnetite at temperatures below 1400 °C, especially under more oxidizing conditions. SEM-BSE images of polished surfaces of the glasses indicate a homogeneous glassy structure and some accessory crystallites a few micrometres in size (Figure 1). It can thus be concluded that – apart from the Fe oxidation state – only minor differences exist in the chemistry and crystal phases present in the glasses.

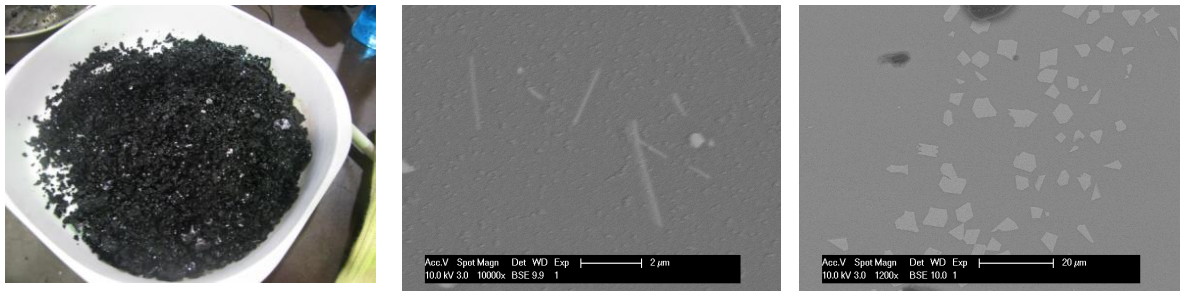


Figure 1: Left: Water quenched glass; Middle: SEM-BSE image of reduced glass with needle-like crystallites in a glassy matrix. Right: SEM-BSE image of oxidized glass with magnetite crystals in glassy matrix.

Synthesis and properties of the inorganic polymer cement

Both glasses were milled in a ball mill using identical milling parameters obtaining a Blaine surface of 1700 cm²/g for both glasses. Mortar bars of 16 x 4 x 4 cm³ were prepared according to EN196-1, using a liquid/glass ratio of 0.5 and a Na-silicate solution of composition (in wt.%) 13.25 SiO₂, 11.63 Na₂O, 75.12 H₂O. Norm CEN sand was added respecting a glass/sand mass ratio of 1/3. The compressive and flexural strength were measured after 2, 7 and 28 days of curing in closed plastic boxes at 20 °C. Results are shown in Figure 2.

Compressive and flexural strength values are lower when compared to previously published data (compressive strength values of 71.7 MPa after 28 days were reached using a similar oxidised vitreous precursor and similar IP synthesis conditions).³ The lower values are explained by the relatively coarser particle size of the milled glass and the differing glass chemistry (lower amount of network-modifiers as Ca in the current system), leading to much slower dissolution and polycondensation. However when comparing the values of the oxidized and reduced glasses, differences are striking, as mortars prepared from the reduced glass show both faster hardening and substantially higher absolute values in both compressive and flexural strength. After two days of curing, mortars prepared with the oxidized glass had not hardened yet, indicating very slow rates of dissolution and/or polycondensation and subsequent polymerisation. Similar behaviour of Fe³⁺-rich precursors was indicated by other authors.⁸ After 7 days, mortars were still wet, strength was sufficient to allow testing, but still very low. After 28 days the samples were hard and dry, but compressive and flexural strength remain considerably low. Mortars prepared from the reduced glass had dried after two days, having strength values double the compressive strength of the oxidized glass samples at 7 and 28 days and 10 times the flexural strength of the oxidized glass at 7 and 28 days.

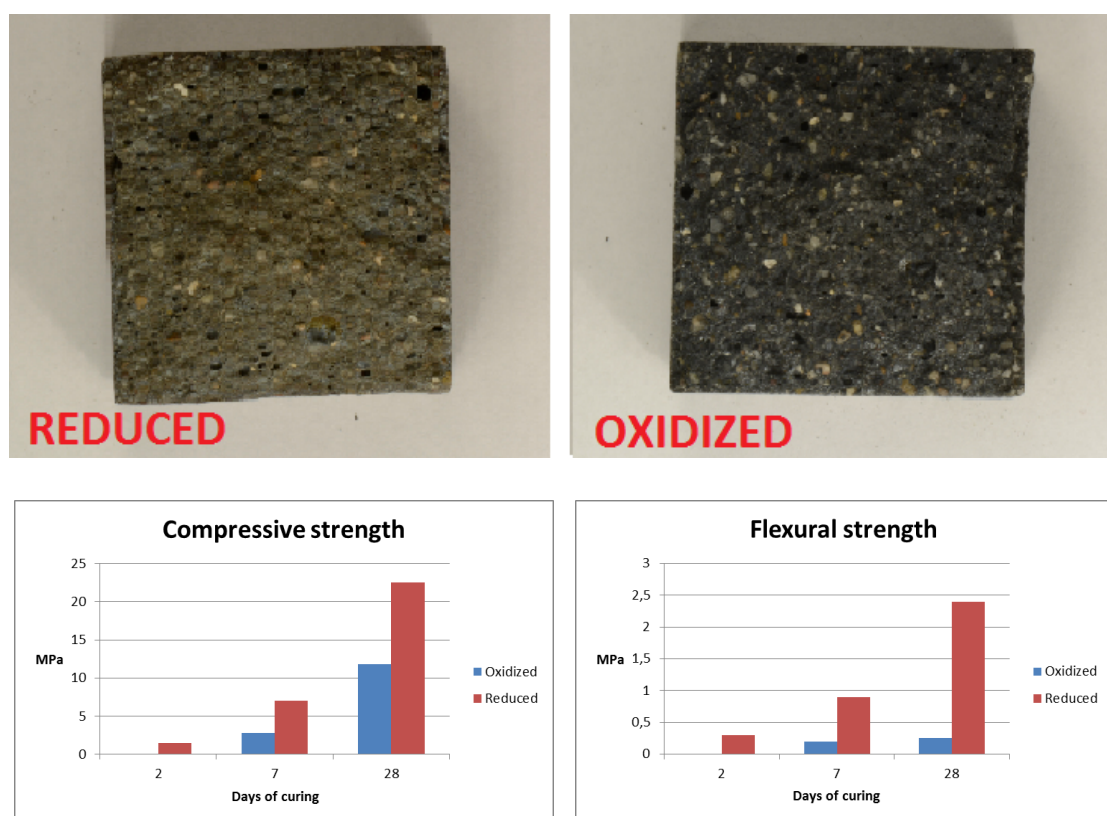


Figure 2: Top: Image of cured inorganic polymer samples from oxidized and reduced glasses. Bottom: Compressive and Flexural strength tested according to 196-1 after 2, 7 and 28 days curing. Sample cross-section is visible that corresponds to 4 x 4 cm².

Considering that the chemistry and crystal phases found in both samples are similar, it is assumed that the oxidation state of Fe is the determining factor that leads to the differing properties. Possible explanations could be either the differing dissolution behaviour of both glasses in the Na-silicate solution, e.g. Fe²⁺, working as a network modifier in the glass, leading to faster glass dissolution, or a differing behaviour during the steps of inorganic polymerisation, e.g. Fe³⁺ forms FeOOH precipitates or is incorporated in octahedral positions in the IP framework that are not cross-linked and do not contribute to strength development, as has suggested in the introduction. Fe²⁺ could possibly have a different behaviour. It could be hypothesised that Fe²⁺ is incorporated in a tetrahedral position that is incorporated in the inorganic polymer network. If this is the case, Fe²⁺ in tetrahedral coordination - even if oxidized to Fe³⁺ in a later stage - could fulfil a similar role as Al, providing crosslinking of silicate chains and resulting in relatively fast formation of a rigid 3D IP structure.

Conclusions

Inorganic polymer (IP) cements can be produced from both reduced and oxidized Fe-rich glasses. When comparing glasses of similar chemistry and glass content, but with differing Fe oxidation state (ferrous Fe^{2+} vs. ferric Fe^{3+}), the produced cement from the ferrous glasses tend to set, dry and harden faster and have better overall mechanical properties compared to the cement prepared from ferrous glasses. One possible hypothesis to interpret the above, is that Fe^{2+} is incorporated in tetrahedral positions in the IP framework and delivers a similar role as Al, i.e. cross linking between silica chains and forming a rigid 3D work. Additional microstructural analyses (e.g. FTIR, Raman, Mössbauer) and microchemical studies are to be performed to evaluate this hypothesis.

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